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Unique properties of $ZnTiF_6 \cdot 6H_2O:Mn^{4+}$ red-emitting hexahydrate phosphor

Ryosuke Hoshino, Shono Sakurai, Toshihiro Nakamura*, Sadao Adachi*

Division of Electronics and Informatics, Faculty of Science and Technology, Gunma University, Kiryu-shi, Gunma 376-8515, Japan

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ABSTRACT

The structural and luminescence properties of $ZnTiF_6 \cdot 6H_2O:Mn^{4+}$ red-emitting hexahydrate phosphor were investigated using X-ray diffraction (XRD) measurement, photoluminescence (PL) analysis, PL excitation spectroscopy, electron paramagnetic resonance, and Raman scattering spectroscopy. The $ZnTiF_6 \cdot 6H_2O:Mn^{4+}$ phosphor exhibited remarkable change in the XRD traces and PL spectra after thermal annealing at temperatures (T_a) below or above ~150°C. After heating below ~150°C, the hexahydrate phosphor showed structural phase transition, probably from the room-ambient stable trigonal symmetry ($R\bar{3}$) to the low-temperature stable monoclinic symmetry ($P2_1/c$). Surprisingly, similar XRD and PL data were obtained when the phosphor was vacuum-evacuated in a cryostat. This is also a novel finding of the present work and is supported by the Raman scattering data. The partially dehydrated state returned to the rehydrated state by putting the sample in room ambient. Annealing above a T_a of ~200°C changed the hexahydrate phosphor to the dehydrated one ($ZnTiF_6:Mn^{4+}$) with the trigonal $R\bar{3}m$ symmetry and gave clearly different PL spectra from its hexahydrate counterpart. Photo-induced degradation in the PL efficiency of $ZnTiF_6 \cdot 6H_2O:Mn^{4+}$ was also observed by exposing the samples to visible–near-UV light and could be explained by the photooxidation and/or disproportionation reactions of the Mn ions.

1. Introduction

Mn^{4+} ion is an efficient activator enabling red or deep red light emission in various host materials [1]. $K_2SiF_6:Mn^{4+}$ phosphor is a good example and is used to obtain efficient red emission [2]. A warm-white light-emitting diode (LED), with color temperature of 3510 K, color rendering index of 90.9, and efficacy of 81.56 lm/W has been demonstrated using this red-emitting phosphor combined with a commercial Ce^{3+}-doped garnet yellow-green phosphor that was mounted on a III–nitride LED chip [3].

The $A^{II}B^{IV}F_6$ hexafluoride family can exist in the hydrate and or anhydrous form. The hydrate form usually has six water molecules. A typical example for the former hexafluoride is $ZnSiF_6 \cdot 6H_2O$ [4,5], while the latter is $BaSiF_6$ [6]. It has been found that $ZnSnF_6 \cdot 6H_2O$ shows dehydration by heating the hexahydrate to ~200°C [7,8]. Further heating above 200°C led to thermal decomposition into metal oxide/fluoride. $A^{II}B^{IV}F_6 \cdot 6H_2O$ hexahydrate material is also unique in the sense of exhibiting structural phase transitions at T_c~150–300 K [9–11]. Like $K_2SiF_6:Mn^{4+}$, $A^{II}B^{IV}F_6:Mn^{4+}$ and $A^{II}B^{IV}F_6 \cdot 6H_2O:Mn^{4+}$ phosphors emit lights in the red spectral region [4–6].

Because of the presence of six water molecules per formula unit in $A^{II}B^{IV}F_6 \cdot 6H_2O$ hexahydrate crystals, it is expected that these hexahydrate materials may exhibit instability on heating or on applying other external perturbations. In fact, we have observed various instabilities and related changes in the $ZnSnF_6 \cdot 6H_2O:Mn^{4+}$ and $K_2SnF_6 \cdot H_2O:Mn^{4+}$ red-emitting phosphor properties [7,8,12]. Recently, Zhong et al. [13] reported the synthesis and optical properties of a new $ZnTiF_6 \cdot 6H_2O:Mn^{4+}$ red-emitting phosphor for use in warm-white LED applications. It is evident that studying the stability of hydrate phosphors is of both scientific interest and technological importance.

The purpose of this study is twofold: (i) to investigate in detail whether structural phase transition occurs in $ZnTiF_6 \cdot 6H_2O$ and (ii) to report unique phosphor properties observed in the $ZnTiF_6 \cdot 6H_2O:Mn^{4+}$ phosphor against thermal annealing and on exposing to vacuum. The hexahydrate phosphors were synthesized using the method of Zhong et al. [13]. Clear structural phase transitions were observed by applying external perturbations such as heating and vacuum evacuation. As expected, the change in the crystal structure caused by phase transition had strong influences

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* Corresponding authors.
E-mail addresses: tnakamura@gunma-u.ac.jp (T. Nakamura), adachi@gunma-u.ac.jp (S. Adachi).

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on the phosphor properties. Novel photo-induced degradation of the luminescence intensity was observed and explained by the photooxidation and/or disproportionation reactions of the Mn ions.

2. Experimental

The Mn^{4+}-activated $ZnTiF_6 \cdot 6H_2O$ phosphor was synthesized from raw materials of ZnF_2, TiO_2, KHF_2, H_2O_2, $KMnO_4$, and HF proposed by Zhong et al. [13]. The body color of the phosphor is yellowish typically observed in the various phosphors doped with Mn^{4+}[1,14]. The synthesized phosphors were ground in an agate mortar and used for various measurements.

The X-ray diffraction (XRD) patterns of the synthesized powders were analyzed by means of XRD spectroscopy using a SmartLab X-ray diffractometer (Rigaku) with Cu $K\alpha$ radiation at $\lambda = 0.1542$ nm. Photoluminescence (PL) measurements were performed using a single monochromator equipped with a charge-coupled device (Princeton Instruments PIXIS 100B) and a He–Cd laser (Kimmon IK3302R-E) at $\lambda_{ex} = 325$ nm as the excitation light source. Temperature dependence of the PL spectra was measured from $T = 20$ to 300 K. PL excitation (PLE) spectra were measured using a fluorescence spectrometer (Hitachi F-4500) at 300 K.

Thermal degradation of the phosphor was studied on an electric hot plate in room air at 50 – 400°C for 1 h. A change in the XRD and PL intensities was examined for the samples before and after vacuum evacuation in a conventional cryostat at $\sim 10^{-5}$ Pa.

A He – Ne laser at 632.8 nm (LASOS LGK 7628), an Ar^+ laser at 488 nm (Showa Optronics GLG3110), and a He – Cd laser at 325 nm (Kimmon IK3302R-E) were used as the light sources of photo-induced degradation in $ZnTiF_6 \cdot 6H_2O:Mn^{4+}$ phosphor. A 50 W continuous Xe lamp was also used as the degradation light source.

EPR measurements were performed to monitor Mn^{4+} spin densities before and after Xe lamp exposure on the phosphor surfaces. An ELEXSYS E500 (Bruker Corp.) X-band ESR spectrometer was used for this purpose at 300 K.

Raman spectrometer consisted of an Ar ion laser at 488 nm (Showa Optronics Corp., GLG 3110) and a charge-coupled device (Princeton Instruments, PIXIS 100B) with an LP02-488RU interference filter (Semrock, Inc.). The Raman scattering measurements were performed under depolarization condition at 300 K.

3. Results and discussion

3.1. *Basic properties of room-ambient stable $ZnTiF_6 \cdot 6H_2O:Mn^{4+}$ phosphor*

Fig. 1 shows the XRD patterns of some Mn^{4+}-activated hexafluorotitanate red-emitting phosphors: (a) $K_2TiF_6:Mn^{4+}$ [15], $BaTiF_6:Mn^{4+}$ [16], and $ZnTiF_6 \cdot 6H_2O:Mn^{4+}$. It should be noted that the first two phosphors exhibit no any clear structural phase transition against temperatures from cryogenic to melting points. All these phosphors crystallize in the trigonal structure with the space groups of $P\bar{3}m1 - D_{3d}^3$ ($K_2TiF_6:Mn^{4+}$), $R\bar{3}m - D_{3d}^5$ ($BaTiF_6$: Mn^{4+}), and $R\bar{3} - C_{3i}^2$ ($ZnTiF_6 \cdot 6H_2O:Mn^{4+}$). The diffraction patterns from the American Society for Testing and Materials (ASTM) cards are shown in the bottom of each figure: (a) K_2TiF_6 (#00-008-0488), (b) $BaTiF_6$ (#01-076-0269), and $ZnTiF_6 \cdot 6H_2O$ (#01–084-1772).

The strongest peak at $2\theta \sim 18.5°$ in Fig. 1(c) is due to the (110) diffraction plane in the $ZnTiF_6 \cdot 6H_2O$ lattice. Summary of various crystal properties, such as crystal class, space group, optical classification, and piezoelectric and optical rotation activity, together with the fundamental Mn^{4+} emission properties, of some Mn^{4+}-activated hexafluoride phosphors, including $K_2TiF_6:Mn^{4+}$ and $BaTiF_6:Mn^{4+}$, is given in Ref. [7]. As expected, the XRD pattern of $ZnTiF_6 \cdot 6H_2O$ is very similar to its isostructural hexafluoride patterns: $ZnSiF_6 \cdot 6H_2O$ [4,5], $ZnGeF_6 \cdot 6H_2O$ [17], and $ZnSnF_6 \cdot 6H_2O$ [7,8].

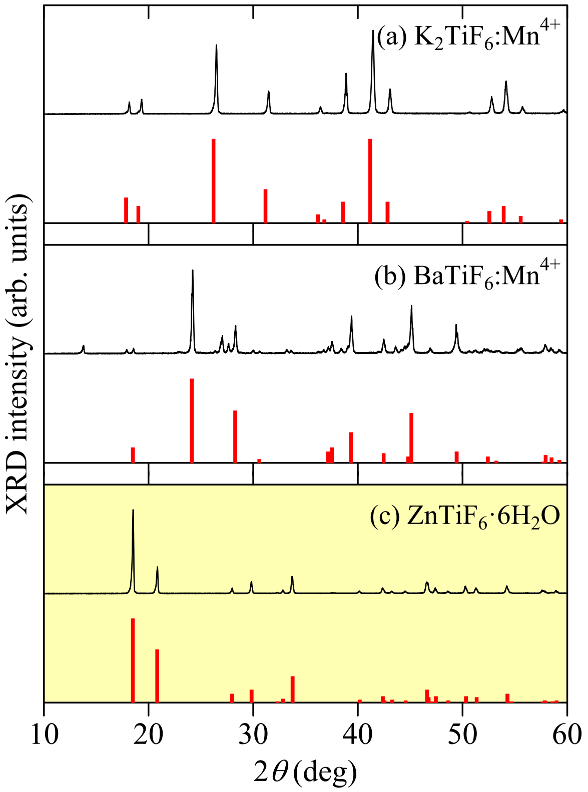

Fig. 1. XRD patterns for some Mn^{4+}-activated hexafluorotitanate red-emitting phosphors: (a) $K_2TiF_6:Mn^{4+}$ [15], $BaTiF_6:Mn^{4+}$ [16], and $ZnTiF_6 \cdot 6H_2O:Mn^{4+}$. All these red-emitting phosphors crystallize in the trigonal structure with the space group symmetries of (a) $P\bar{3}m1$ (b) $R\bar{3}m$, and (c) $R\bar{3}$. The diffraction patterns taken from the ASTM cards are shown in the bottom of each figure: (a) K_2TiF_6 (#00–008-0488), (b) $BaTiF_6$ (#01-076-0269), and $ZnTiF_6 \cdot 6H_2O$ (#01-084-1772).

Fig. 2 shows the PL and PLE spectra for (a) $K_2TiF_6:Mn^{4+}$ [15], $BaTiF_6:Mn^{4+}$ [16], and $ZnTiF_6 \cdot 6H_2O:Mn^{4+}$ measured at 300 K. All these phosphors have the luminescence spectra of sharp red emission peaks as typically observed in various Mn^{4+}-activated phosphors, such as $CaAl_{12}O_{19}:Mn^{4+}$ [18], α-$LiAlO_2:Mn^{4+}$[19], $Ca_{14}Zn_6Al_{10}O_{35}:Mn^{4+}$ [20], $La_2MgTiO_6:Mn^{4+}$ [21], and $K_2Ge_4O_9$: Mn^{4+} [22]. Brik and Srivastava [23] reported a review paper of the luminescence properties of Mn^{4+} ions in a number of phosphors. The sharp red emission peaks in Fig. 2 are ascribed to the ${}^2E_g \rightarrow {}^4A_{2g}$ transition of the $3d^3$ electrons in the MnF_6^{2-} octahedron of the hexafluorotitanate hosts.

The PLE spectra in Fig. 2 reveal the two absorption bands at ~470 nm and ~360 nm. These absorption bands are assigned to the ${}^4A_{2g} \rightarrow {}^4T_{2g}$ (~470 nm) and ${}^4A_{2g} \rightarrow {}^4T_{1g}$ transitions (~360 nm) in the Mn^{4+} ions. At low temperatures, these absorption bands exhibit a multiple-peak structure caused by the vibronic quanta at the excited state of the $3d^3$ electrons in the MnF_6^{2-} octahedron. Such multiple-peak structure can be well explained by the configurational-coordinate model based on the Franck – Condon principle [24]:

$$I_{PLE}(E) = \sum_n I_n^{ex}(n)\ \exp\left[- \frac{(E - E_{ZPL} - nh\nu_{p,ex})^2}{2\sigma_{ex}{}^2} \right] \quad (1)$$